

AD

EDGEWOOD ARSENAL
TECHNICAL REPORT

EATR 4568

PROBES OF NONREACTIVE ENVIRONMENT
III. THEORETICAL ASPECTS OF PYRIDINIUM
IODIDE CHARGE-TRANSFER ABSORPTION

by

Raymond A. Mackay

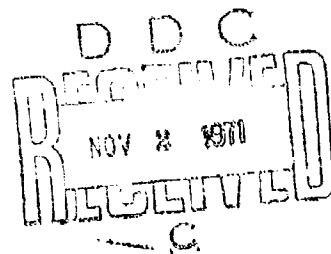
Edward J. Poziomek

October 1971



Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va 22151

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Physical Research Laboratory
Edgewood Arsenal, Maryland 21010



ADDITIONAL FOR	
OFSTI	WHITE SECTION <input checked="" type="checkbox"/>
DDO	BLUE SECTION <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION AVAILABILITY CODES	
DIST.	AKKIL. AND OF SPECIAL

Distribution Statement

Approved for public release; distribution unlimited.

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when no longer needed. Do not return it to the originator.

UNCLASSIFIED

Security Classification		
DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION
CO, Edgewood Arsenal ATTN: SMUEA-R-PRE Edgewood Arsenal, Maryland 21010		UNCLASSIFIED
		2b. GROUP
		NA
3. REPORT TITLE		
PROBES OF NONREACTIVE ENVIRONMENT. III. THEORETICAL ASPECTS OF PYRIDINIUM IODIDE CHARGE-TRANSFER ABSORPTION		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
This work was performed in 1970.		
5. AUTHOR(S) (First name, middle initial, last name)		
Edward J. Poziomek, and Raymond A. Mackay		
6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
October 1971	20	15
8a. CONTRACT OR GRANT NO.	8b. ORIGINATOR'S REPORT NUMBER(S)	
	EATR 4568	
9. PROJECT NO.	9c. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
f. Task No. 1B662710AD2901		
10. DISTRIBUTION STATEMENT		
Approved for public release; distribution unlimited.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY	
	NA	
13. ABSTRACT		
<p>Pyridinium iodide salts possess iodide to ring charge-transfer (c-t) absorption; two c-t bands are generally observed in nonpolar solvents. The existence of two bands is important for the researcher in detection because the absolute and relative energies of these bands could be a useful indication of changes to ring substituents and environment surrounding the ring. A question exists, however, as to whether the higher energy c-t band arises from an excited state of the donor or from a higher energy state of the acceptor. Self-consistent extended Hückel calculations have been performed for the unsubstituted and the 2-, 3-, and 4-cyano (and acetyl) pyridinium ions. The calculated difference between the energy of the first (lowest) and second (next highest) vacant molecular orbital of the pyridinium ion is in good agreement with the observed separation of the two c-t bands in methylene chloride. This supports other experimental results, which indicate that the second c-t band does not arise from the excited state ($^2P_{1/2}$) of the iodine atom. These and other results of the calculation are discussed in terms of various experimental parameters.</p>		
14. KEYWORDS		
Defense systems	Molecular complexes	
Spectroscopy	Electron affinity	
Pyridinium iodides	Substituent constants	
Charge-transfer	Solvent	
Molecular orbitals	Environment	
	Army research	

DD FORM 1473

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

19

UNCLASSIFIED

Security Classification

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Defense systems						
Spectroscopy						
Pyridinium iodides						
Charge-transfer						
Molecular orbitals						
Molecular complexes						
Electron affinity						
Substituent constants						
Solvent						
Environment						
Army research						

UNCLASSIFIED

Security Classification

EDGEWOOD ARSENAL TECHNICAL REPORT
EATR 4568

PROBES OF NONREACTIVE ENVIRONMENT
III. THEORETICAL ASPECTS OF PYRIDINIUM
IODIDE CHARGE-TRANSFER ABSORPTION

by

Raymond A. Mackay

Drexel University

and

Edward J. Poziomek

Defensive Research Department

October 1971

Approved for public release; distribution unlimited.

Task 1B662710AD2901

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Physical Research Laboratory
Edgewood Arsenal, Maryland 21010

DIGEST

Pyridinium iodide salts possess iodide to ring charge-transfer (c-t) absorption; two c-t bands are generally observed in nonpolar solvents. The existence of two bands is important for the researcher in detection because the absolute and relative energies of these bands could be a useful indication of changes to ring substituents and environment surrounding the ring. A question exists, however, as to whether the higher energy c-t band arises from an excited state of the donor or from a higher energy state of the acceptor. Self-consistent extended Hückel calculations have been performed for the unsubstituted and the 2-, 3-, and 4-cyano (and acetyl) pyridinium ions. The calculated difference between the energy of the first (lowest) and second (next highest) vacant molecular orbital of the pyridinium ion is in good agreement with the observed separation of the two c-t bands in methylene chloride. This supports other experimental results, which indicate that the second c-t band does not arise from the excited state ($^2P_{1/2}$) of the iodine atom. These and other results of the calculation are discussed in terms of various experimental parameters.

FOREWORD

The work described in this report was authorized under Task 1B662710AD2901, Chemical Detection and Identification Technology, Detection and Identification Concepts. The work was performed in 1970.

Reproduction of this document in whole or in part is prohibited except with permission of the Commanding Officer, Edgewood Arsenal, ATTN: SMUEA-TS-TIT, Edgewood Arsenal, Maryland 21010; however, DDC and the National Technical Information Service are authorized to reproduce the document for United States Government purposes.

Acknowledgments

The authors wish to express their appreciation to Dr. George Clarke and Dr. Barry Kalman for use of their program and for assistance in the performance of the calculations, and to Mr. Phillip Knorr for technical assistance. Especial thanks are due Dr. Kalman for many helpful discussions.

CONTENTS

	Page
I. INTRODUCTION	7
II. CALCULATIONS AND EXPERIMENTATION	7
III. RESULTS AND DISCUSSION	7
A. Band Energies	7
B. Electron Affinity	10
C. Substituent Constants	10
IV. CONCLUSIONS	11
LITERATURE CITED	13
DISTRIBUTION LIST	15

PRECEDING PAGE BLANK

PROBES OF NONREACTIVE ENVIRONMENT

III. THEORETICAL ASPECTS OF PYRIDINIUM IODIDE CHARGE-TRANSFER ABSORPTION

I. INTRODUCTION.

The first (long wavelength) electronic absorption band of pyridinium iodide salts has been studied extensively. It arises from charge-transfer from iodide ion to the pyridinium ion.^{1,2} In nonpolar solvents a second c-t band, at shorter wavelength than the first, is observed and has been ascribed to the first excited state of the iodine atom ($^2P_{3/2}$).³ Recent experimental results indicate that the second band may in fact result from charge-transfer to the second vacant molecular orbital of the pyridinium ion.^{2,4} We have therefore performed self-consistent extended Hückel (SCEH) calculations on various pyridinium ions and compared the results with experimental parameters including c-t band energies.

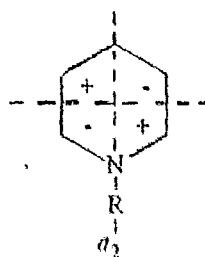
II. CALCULATIONS AND EXPERIMENTATION.

The calculations were performed by the method suggested by Harris⁵ using a modified procedure of Kalman and Clarke.⁶ All valence orbitals and electrons were included. The electron affinities of the pyridinium ions were taken as the negative of the ionization potential of the corresponding pyridinyl radicals. The band energies and the rate constants were determined in methylene chloride.²

III. RESULTS AND DISCUSSION.

A. Band Energies.

The lowest unoccupied molecular orbital (LUMO) in benzene is a doubly degenerate π orbital (e_{2g} in D_{6h}); on going to pyridine or pyridinium ion, it splits into b_1 and a_2 (in C_{2v}). These orbitals are shown below. The dotted line indicates the modes.



¹Kosower, E. M., and Skorcz, J. A. Pyridinium Complexes. III. Charge-Transfer Bands of Polyalkylpyridinium Iodides. *J. Amer. Chem. Soc.* **82**, 2195 (1960).

²Mackay, R. A., Landolph, J. R., and Pozlomek, E. J. Experimental Evidence Concerning the Nature of the Two Charge-Transfer Bands in Pyridinium Iodides. *J. Amer. Chem. Soc.* **93** (1971), and references therein.

³Kosower, E. M., Skorcz, Schwarz, W. M., Jr., and Patton, J. W. Pyridinium Complexes. I. The Significance of the Second Charge-Transfer Band of Pyridinium Iodides. *J. Amer. Chem. Soc.* **82**, 2188 (1960).

⁴Verhoeven, J. W., Dirks, I. P., and de Boer, Th. J. Studies of Inter- and Intra-Molecular Donor-Acceptor Interactions. II. Intermolecular Charge Transfer Involving Substituted Pyridinium Ions. *Tetrahedron* **25**, 3395 (1969).

⁵Harris, F. E. Self-Consistent Methods in Hückel Theory. *J. Chem. Phys.* **48** 4027 (1968).

⁶Kalman, B., and Clarke, G. *J. Chem. Phys.* (1971) in press.

PRECEDING PAGE BLANK

The lowest energy orbital has been assigned as b_1 by Kosower and Poziomek⁷ on the basis of infrared evidence and by Verhoeven⁸ on the basis of some simple Hückel linear combination of atomic orbitals-molecular orbitals (LCAO-MO) calculations. Our SCEH calculations confirm these assignments. Both orbitals are essentially π in character; the highest filled MO is mixed but is largely σ (in the plane). The energy separation between the b_1 and a_2 orbitals depends on the nature and position of the substituent on the ring. The first c-t band arises from donation of an electron from iodide into the b_1 orbital of the pyridinium ring. If the second band arises from donation into a_2 , then the energy difference between the two observed c-t bands (ΔE_{c-t}) should be related to the energy difference between the a_2 and b_1 MO's.

Although these are orbital rather than state energies (i.e., configuration interaction has not been included), it is to be expected that the additional terms will be largely self-canceling in ΔE_{c-t} because of the nature of the transitions and the similarity of the two acceptor MO's.

The geometry used for the 1-methyl group was such that one hydrogen atom was in the plane perpendicular to the ring passing through the nitrogen and the 4-position. Except for the acetyl substituents, the remaining geometry was fixed. The acetyl was positioned with the carbonyl oxygen in the plane of the ring.

As may be seen from the results in table I, there is good qualitative agreement between the calculated and experimental values of ΔE_{c-t} . For all but the 3-substituted ions, the quantitative agreement is excellent. The calculated values for the *meta*-substituted species are somewhat low, but still good considering that the energy gap is now fairly small. It may be that the parameters used⁶ are not quite optimal for this system.

The difference in energy between the $^2P_{1/2}$ and $^2P_{3/2}$ states of the iodine atom is 21.7 kcal mole⁻¹.² If the second c-t band also arises from donation into the b_1 orbital of the ring, but with the iodine atom being left in its first excited ($^2P_{1/2}$) state, then in the absence of any strong interactions ΔE_{c-t} should be about 22 kcal mole⁻¹ regardless of the substituent. In other words, ΔE_{c-t} should be approximately independent of the acceptor, as is observed in alkali iodide c-t spectra. In tropylium iodide, which has only one (doubly degenerate) acceptor orbital, two iodide to ring c-t bands are observed in CH_2Cl_2 with a ΔE_{c-t} of 19.9 kcal mole⁻¹.⁹ The spectra of tropylium chloride and bromide substantiate that the two bands do arise from the $^2P_{3/2}$ and $^2P_{1/2}$ states of iodine.¹⁰ This is in accord with the expectation that ΔE_{c-t} should not vary more than a few kcal mole⁻¹ from the gas phase $^2P_{1/2} - ^2P_{3/2}$ separation. Thus, one should expect to observe three c-t bands in the pyridinium iodide spectra, one about 21 kcal mole⁻¹ higher than the first (lowest energy) band, and another varying between 10 and 30 kcal mole⁻¹ higher than the first, depending on the substituent, and its position. However, only two bands have been definitely observed.² In fact, there should be four bands, the last corresponding to transfer of an electron into the second vacant MO of the pyridinium ring, leaving the iodine in the $^2P_{1/2}$ state. However, this band would be "buried" under the intense local transitions of the ring.

⁷ Kosower, E. M., and Poziomek, E. J. Stable Free Radicals. I. Isolation and Distillation of 1-Ethyl-4-carbomethoxy-pyridinyl. J. Amer. Chem. Soc. 86, 5515 (1964).

⁸ Verhoeven, J. W. Intramolecular Electron Donor-Acceptor Interaction in N-Alkyl-Pyridinium Ions. Thesis. Laboratorium voor Organische Scheikunde der Universiteit van Amsterdam. 1969.

⁹ Kosower, E. M. The Solvent Sensitivity of the Charge-Transfer Band of Tropylium Iodide. J. Org. Chem. 29, 956 (1964).

¹⁰ Harmon, K. M., Cummings, F. E., Davis, D. A., and Diestler, D. J. Carbonium Ion Salts. V. The Spectra and Decomposition of Tropylium Halides in Methylene Chloride. J. Amer. Chem. Soc. 84, 3349 (1962).

Table I. Charge-Transfer Transition Energies for Several 1-Methylpyridinium Iodides

Ring substituent	E_{t1}^a	E_{t2}^a	ΔE_{c-t}^b	
			Found	Calcd
4-CN	58.2	85.3	27.1	29.0
4-COCH ₃	63.8	92.5	28.7	30.8
2-CN	59.8	81.2	21.6	20.1
2-COCH ₃	64.7	87.2	22.5	19.7
1-CH ₃	76.7	98.2	21.5	19.5
3-CN	65.0	79.0	14.0	7.2
3-COCH ₃	70.6	80.8	10.2	7.1

^a E_{t1} and E_{t2} are the first and second c-t band energies respectively in kcal mole⁻¹ (precision ± 0.2 kcal mole⁻¹; accuracy ± 0.4 kcal mole⁻¹) as determined in CH₂Cl₂.

^b ΔE_{c-t} (Found) = $E_{t2} - E_{t1}$. ΔE_{c-t} (Calcd) = $E(a_2) - E(b_1)$, in kcal mole⁻¹.

The energy difference for 2,4,6-trimethylpyrylium iodide c-t bands (in CHCl₃) was found to be 14.5 kcal mole⁻¹.¹¹ Here, however, local transitions are close in energy to the c-t bands and can interact with them. In particular, the $n-\pi^*$ transition can interact with the c-t band, which leaves iodine in the $^2P_{1/2}$ state, possibly giving it intensity and shifting it to lower energy. In contrast to the pyrylium ion, however, the pyridinium ion does not possess a lone pair of electrons, and this interaction is not possible. Thus, the absence of the third band is puzzling. A possible explanation for the failure to observe this c-t band is that it has been reduced in intensity because of what may be considered as a "ligand field" splitting of the iodine 5p orbitals by the pyridinium ion. The space part of the wave functions for the $^2P_{3/2}$ and $^2P_{1/2}$ states of iodine contain contributions from the p_x , p_y , and p_z orbitals. Assuming that the electron transferred from the iodide ion to the ring in the c-t process is donated essentially from an iodine 5p orbital, the relative contribution of the p_x , p_y , and p_z orbitals to the overall transition dipole moment may be calculated. For a model in which the iodide ion is located on the z-axis above the center of a "benzene" ring (idealized C_{6v} symmetry), the contribution of p_x and p_y are equal and very much greater than that of p_z . Calculations show that this is still true even when the actual pyridinium ion is used and the iodide ion is located over the position of minimum electrostatic potential energy, which is somewhat displaced from the center of the ring.

For zero ligand field splitting (Δ), the two c-t bands, due to the iodine being left in the $^2P_{3/2}$ and $^2P_{1/2}$ states, are thus of comparable intensity. In the limit of $\Delta \gg \xi$ (spin-orbit coupling constant), the $^2P_{3/2}$ and $^2P_{1/2}$ states go over to two other states, designated 2E and 2A respectively. The 2E state contains only p_x and p_y , whereas 2A contains only p_z . In this case, the c-t transition leaving iodine in the 2A state has negligible intensity [in the idealized case (C_{6v}), zero intensity] compared to the lower energy transition, which leaves iodine in the 2E state. There is some experimental support for this explanation from other c-t spectra. In the case of tropylium iodide, the higher energy c-t band is less intense than the lower energy one;⁹ for the bromide, both bands (although not completely resolved) are clearly of comparable intensity. The higher energy band is considerably less intense in 2,6-dichlorobenzylquinolinium iodide,¹² which might be

¹¹Balaban, A. T., Mocanu, M., and Simon, Z. Charge-transfer Spectra of Pyrylium Iodides. *Tetrahedron* 20, 119 (1964).

¹²Briegleb, G., Jung, W., and Herre, W. Anionen-und Lösungsmittel-Abhängigkeit eines interionaren Elektronenaustausches in Ionenpaaren (am Beispiel von Salzen des N,2,6-Dichlorbenzylchinoliniums). *Z. Phys. Chem. Neue Folge* 38, 253 (1963).

expected to have a "ligand field strength" closer to that of the pyridinium ion. In the case of gaseous iodide, both bands would, as observed, be expected to be of comparable intensity regardless of the value of Δ because of the spherical symmetry of the acceptor orbital on the alkali metal ion. Thus, the relative intensities of the possible c-t transitions between iodide ion and an acceptor will depend on the nature of the acceptor orbital(s), the geometry of the complex, and the ligand field strength of the acceptor species.

B. Electron Affinity.

The electron affinity (EA) of the pyridinium ion has been taken as equal to the negative of the calculated ionization potential (IP) of the pyridinyl radical. Although the calculation is capable of giving absolute values of the IP within 1.0 to 1.5 ev, the relative values for different positions of the same substituent are considerably better. A plot of E_{t1} versus EA (data given in table II) shows the correct general trend. The individual correlations for the 2-, 3-, and 4-CN or COCH₃ substituted ions are quite good.

C. Substituent Constants.

Correlation of σ substituent constants with E_{t1} (in CHCl₃) has been reported by Kosower and Skorecz¹³ for 4-CN, 4-COOCH₃, 3-COOCH₃, H-, 3-CH₃, and 4-CH₃ substituted pyridinium iodides; σ^- values were used for the 4-substituents that are electron withdrawing. Similarly, there is a good correlation of σ substituent constants with E_{t1} (obtained in CH₂Cl₂) for the compounds listed in table III.

Table II. Calculated Electron Affinities for Several 1-Methylpyridinium Iodides

Ring substituent	EA ^a	E_{t1} ^b
1-CH ₃	7.83	3.32
3-CN	7.96	2.86
3-COCH ₃	8.54	3.06
2-COCH ₃	8.73	2.80
4-COCH ₃	8.76	2.78
2-CN	8.23	2.58
4-CN	8.32	2.52
Tl ⁺ ^c	8.85	2.16 ^d

^aElectron affinity.

^bFirst c-t band as observed in CH₂Cl₂.

^cTropylium ion.

^dCalculated from datum from Kosower, E.M. The Solvent Sensitivity of the Charge-Transfer Band of Tropylium Iodide. J. Org. Chem. 29, 956 (1964).

¹³Kosower, E. M., and Skorecz, J. A. In *Advances in Molecular Spectroscopy*, p 413. Pergamon Press, New York, New York, 1962.

Table III. Comparison of the Energy of the First c-t Band (E_{ct}) of Various Pyridinium Iodides (in CH_2Cl_2) With σ Substituent Constants and Calculated Charges (Q_N) on the Pyridinium Nitrogen

Ring substituent	E_{ct}^a kcal/mole	σ_m^b	σ_p^b	σ_p^{c}	Q_N^d
H	76.7	0	0	0	1.00
3-CN	65.6	+0.56	-	-	1.54
2-CN	60.1	-	-	-	1.77
4-CN	58.5	-	+0.66	+1.00	1.57
3-COCH ₃	70.6	+0.38	-	-	1.29
2-COCH ₃	64.7	-	-	-	1.31
4-COCH ₃	63.8	-	+0.50	+0.87	1.37
4-CH ₃	80.7 ^e	-	-0.17	-	-
3-CH ₃	78.0 ^e	-0.069	-	-	-
3-COOC ₂ H ₅	71.3	+0.37	-	-	-
4-COOC ₂ H ₅	65.2	-	+0.45	+0.68	-
2-COOC ₂ H ₅	67.8	-	-	-	-

^aFrom Mackay, R. A., Landolph, J. R., and Poziolek, E. J. Experimental Evidence Concerning the Nature of the Two Charge-Transfer Bands in Pyridinium Iodides. *J. Amer. Chem. Soc.* 93 (1971).

^bFrom Hine, J. *Physical Organic Chemistry*. p. 87. McGraw-Hill Book Company, Inc., New York, New York. 1962.

^cFrom Jaffe, H. H. A Reexamination of the Hammett Equation. *Chem. Rev.* 53, 191 (1953).

^dThe calculated charges on nitrogen are normalized to the unsubstituted 1-methyl pyridinium ion.

^eFrom CHCl_3 data as "corrected" to CH_2Cl_2 . Data from Kosower, E. M., and Skorez, J. A. *In Advances in Molecular Spectroscopy*. p 413. Pergamon Press, New York, New York. 1962.

Steric hindrance by a substituent towards iodide ion approaching the pyridinium ring would not be expected to vary appreciably with ring position. This allows an estimate of ortho σ^- values from c-t transitions observed with the 2-substituted compounds. For example, the ortho σ^- values for 2-COOC₂H₅, 2-COCH₃, and 2-CN as estimated from a plot of the data in table III are +0.48, +0.65, and +0.89 respectively. These fall in between the values of σ_p and σ^- for the corresponding *p*-substituent.

A reasonable correlation also exists between σ values (σ_p and σ_m) and the calculated charges on the nitrogen (Q_N). However, from a plot of these data (given in table III) and the calculated values of Q_N for the 2-substituents, σ_o for the CN appears to be larger than $\sigma_p\text{-CN}$, whereas $\sigma_o\text{-COCH}_3$ is less than $\sigma_p\text{-COCH}_3$ and approximately equal to $\sigma_m\text{-COCH}_3$. Though the data are interesting, their interpretation in terms of the various possible effects is difficult to achieve satisfactorily without additional results with more compounds.

IV. CONCLUSIONS.

SCEH calculations for 1-methylpyridinium ion and 2-, 3-, and 4-cyano (and acetyl) 1-methylpyridinium ions give data on energy differences between the lowest and next highest vacant molecular orbitals of the pyridinium ion, which are in good agreement with the observed separation

of the two pyridinium-iodide c-t bands in methylene chloride. This result supports previous indications that the higher energy c-t band results from charge-transfer to the second vacant molecular orbital of the pyridinium ion.

Calculated electron affinities of the pyridinium ions show expected trends in plots with the low energy pyridinium-iodide c-t transition. A reasonable correlation was also found to exist between σ values (σ_p and σ_m) and the calculated charges on the pyridinium nitrogen.

A possible explanation for the failure to observe three c-t bands has been proposed, which, if valid, allows prediction of relative intensities from simple group theoretical considerations using idealized symmetry.

LITERATURE CITED

1. Kosower, E. M., and Skorecz, J. A. Pyridinium Complexes. III. Charge-Transfer Bands of Polyalkylpyridinium Iodides. *J. Amer. Chem. Soc.*, **82**, 2195 (1960).
2. Mackay, R. A., Landolph, J. R., and Poziomek, E. J. Experimental Evidence Concerning the Nature of the Two Charge-Transfer Bands in Pyridinium Iodides. *J. Amer. Chem. Soc.* **93** (1971).
3. Kosower, E. M., Skorecz, Schwarz, W. M., Jr., and Patton, J. W. Pyridinium Complexes. I. The Significance of the Second Charge-Transfer Band of Pyridinium Iodides. *J. Amer. Chem. Soc.* **82**, 2188 (1960).
4. Verhoeven, J. W., Dirkx, I. P., and de Boer, Th. J. Studies of Inter- and Intra-Molecular Donor-Acceptor Interactions. II. Intermolecular Charge-Transfer Involving Substituted Pyridinium Ions. *Tetrahedron*, **25**, 3395 (1969).
5. Harris, F. E. Self-Consistent Methods in Hückel Theory. *J. Chem. Phys.*, **48**, 4027 (1968).
6. Kalman, B., and Clarke, G. *J. Chem. Phys.* (1971) in press.
7. Kosower, E. M., and Poziomek, E. J. Stable Free Radicals. I. Isolation and Distillation of 1-Ethyl-4-carbomethoxypyridinyl. *J. Amer. Chem. Soc.* **86**, 5515 (1964).
8. Verhoeven, J. W. Intramolecular Electron Donor-Acceptor Interaction in N-Alkyl-Pyridinium Ions. Thesis. Laboratorium voor Organische Scheikunde der Universiteit van Amsterdam. 1969.
9. Kosower, E. M. The Solvent Sensitivity of the Charge-Transfer Band of Tropylium Iodide. *J. Org. Chem.* **29**, 956 (1964).
10. Harmon, K. M., Cummings, F. E., Davis, D. A., and Diestler, D. J. Carbonium Ion Salts. V. The Spectra and Decomposition of Tropylium Halides in Methylene Chloride. *J. Amer. Chem. Soc.* **84**, 3349 (1962).
11. Balaban, A. T., Mocanu, M., and Simon, Z. Charge-Transfer Spectra of Pyrylium Iodides. *Tetrahedron*, **20**, 119 (1964).
12. Briegleb, G., Jung, W., and Herre, W. Anionen-und Lösungsmittel-Abhängigkeit eines interionaren Elektronenaustausches in Ionenpaaren (am Beispiel von Salzen des N-2,6-Dichlorbenzylchinoliniums). *Z. Phys. Chem. Neue Folge*, **38**, 253 (1963).
13. Kosower, E. M., and Skorecz, J. A. *In Advances in Molecular Spectroscopy*. p 413. Pergamon Press, New York, New York. 1962.
14. Hine, J. *Physical Organic Chemistry*. p 87. McGraw-Hill Book Company, Inc., New York, New York. 1962.
15. Jaffé, H. H. A Reexamination of the Hammett Equation. *Chem. Rev.* **53**, 191 (1953).